UNITED STATES PATENT AND TRADEMARK OFFICE

I, Neil Thomas SIMPKIN BA,

Deputy Managing Director of RWS Group Ltd UK Translation Division, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

- 1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
- 2. That the translator responsible for the attached translation is well acquainted with the German and English languages.
- 3. That the attached is, to the best of RWS Group Ltd knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in Germany on 14 November 2003 under the number 103 53 280.3 and the official certificate attached thereto.
- 4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

For and on behalf of RWS Group Ltd

The 6th day of October 2009

Combination of active substances with insecticidal properties

The invention relates to novel insecticidal active compound combinations consisting, firstly, of known anthranilamides and, secondly, of further known insecticidally active compounds, which combinations are highly suitable for controlling animal pests, such as insects.

It is already known that certain anthranilamides have insecticidal properties (WO 01/70671, WO 02/094791, WO 03/015519, WO 03/016284, WO 03/015518, WO 03/024222, WO 03/016282, WO 03/016283, WO 03/062226, WO 03/027099).

The generic formulae and definitions described in these publications and the individual compounds described therein are expressly incorporated herein by way of reference.

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Furthermore, it is already known that numerous heterocycles, organotin compounds, benzoylureas and pyrethroids have insecticidal and acaricidal properties (cf. WO 93/22297, WO 93/10083, DE-A 26 41 343, EP-A 347 488, EP-A 210 487, US 3,364,177 and EP-A 234 045). However, the activity of these compounds is likewise not always satisfactory.

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It has now been found that mixtures of anthranilamides of the formula (I)

in which

A¹ and A² independently of one another represent oxygen or sulfur,

20 X¹ represents N or CR¹⁰,

represents hydrogen or represents in each case optionally mono- or polysubstituted C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl or C₃-C₆-cycloalkyl, where the substituents independently of one another may be selected from the group consisting of R⁶, halogen, cyano, nitro, hydroxyl, C₁-C₄-alkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfinyl, C₂-C₆-cycloalkylamino, C₂-C₈-dialkylamino, C₃-C₆-cycloalkylamino, (C₁-C₄-alkyl)C₃-C₆-cycloalkylamino and R¹¹,

 R^3

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R² represents hydrogen, C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, C₃-C₆-cycloalkyl, C₁-C₄-alkoxy, C₁-C₄-alkylamino, C₂-C₈-dialkylamino, C₃-C₆-cycloalkylamino, C₂-C₆-alkoxy-carbonyl or C₂-C₆-alkylcarbonyl,

represents hydrogen, R¹¹ or represents in each case optionally mono- or polysubstituted C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, C₃-C₆-cycloalkyl, where the substituents independently of one another may be selected from the group consisting of R⁶, halogen, cyano, nitro, hydroxyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₂-C₆-alkoxycarbonyl, C₂-C₆-alkylcarbonyl, C₃-C₆-trialkylsilyl, R¹¹, phenyl, phenoxy and a 5- or 6-membered heteroaromatic ring, where each phenyl, phenoxy and 5- or 6-membered heteroaromatic ring may optionally be substituted and where the substituents independently of one another may be selected from one to three radicals W or one or more radicals R¹², or

R² and R³ may be attached to one another and form the ring M,

 R^4 represents hydrogen, C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, C₃-C₆-cycloalkyl, C₁-C₆-15 haloalkyl, C2-C6-haloalkenyl, C2-C6-haloalkynyl, C3-C6-halocycloalkyl, halogen, cyano, nitro, hydroxyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-haloalkylthio, C₁-C₄-haloalkylsulfinyl, C₁-C₄-haloalkylsulfonyl, C₁-C₄-alkylamino, C₂-C₈-dialkylamino, C₃-C₆-cycloalkylamino, C₃-C₆-trialkylsilyl or represents in each case optionally mono- or polysubstituted phenyl, benzyl or phenoxy, where the substituents independently of one another may be selected from the group 20 consisting of C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₃-C₆-cycloalkyl, C₁-C₄-haloalkyl, C2-C4-haloalkenyl, C2-C4-haloalkynyl, C3-C6-halocycloalkyl, halogen, cyano, nitro, C1-C4alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄alkylamino, C₂-C₈-dialkylamino, C₃-C₆-cycloalkylamino, C₃-C₆-(alkyl)cycloalkylamino, C₂-C₄-alkylcarbonyl, C₂-C₆-alkoxycarbonyl, C₂-C₆-alkylaminocarbonyl, C₃-C₈-dialkyl-25 aminocarbonyl and C₃-C₆-trialkylsilyl,

R⁵ and R⁸ in each case independently of one another represent hydrogen, halogen or represent in each case optionally substituted C₁-C₄-alkyl, C₁-C₄-haloalkyl, R¹², G, J, -OJ, -OG, -S(O)_p-J, -S(O)_p-G, -S(O)_p-phenyl, where the substituents independently of one another may be selected from one to three radicals W or from the group consisting of R¹², C₁-C₁₀-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, C₁-C₄-alkoxy and C₁-C₄-alkythio, where each substituent may be substituted by one or more substituents independently of one another selected from the group consisting of G, J, R⁶, halogen, cyano, nitro, amino, hydroxyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-haloalkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-alkylamino, C₂-C₈-dialkylamino, C₃-C₆-trialkylsilyl, phenyl and phenoxy, where each phenyl or phenoxy ring

- may optionally be substituted and where the substituents independently of one another may be selected from one to three radicals W or one or more radicals R¹²,
- in each case independently of one another represent a 5- or 6-membered nonaromatic carbocyclic or heterocyclic ring which optionally contains one or two ring members from the group consisting of C(=O), SO and S(=O)₂ and which may optionally be substituted by one to four substituents independently of one another selected from the group consisting of C₁-C₂-alkyl, halogen, cyano, nitro and C₁-C₂-alkoxy, or independently of one another represent C₂-C₆-alkenyl, C₂-C₆-alkynyl, C₃-C₇-cycloalkyl, (cyano)C₃-C₇-cycloalkyl, (C₁-C₄-alkyl)C₃-C₆-cycloalkyl, (C₃-C₆-cycloalkyl)C₁-C₄-alkyl, where each cycloalkyl, (alkyl)cycloalkyl and (cycloalkyl)alkyl may optionally be substituted by one or more halogen atoms,
 - J in each case independently of one another represent an optionally substituted 5- or 6-membered heteroaromatic ring, where the substituents independently of one another may be selected from one to three radicals W or one or more radicals R¹²,
- 15 R^6 independently of one another represent $-C(=E^1)R^{19}$, $-LC(=E^1)R^{19}$, $-C(=E^1)LR^{19}$, $-LC(=E^1)LR^{19}$, $-OP(=Q)(OR^{19})_2$, $-SO_2LR^{18}$ or $-LSO_2LR^{19}$, where each E^1 independently of the others represents O, S, N-R¹⁵, N-OR¹⁵, N-N(R¹⁵)₂, N-S=O, N-CN or N-NO₂,
 - $R^7 \qquad \text{represents hydrogen, C_1-C_4-alkyl, C_1-C_4-haloalkyl, halogen, C_1-C_4-alkoxy, C_1-C_4-haloalkyl, halogen, C_1-C_4-alkoxy, C_1-C_4-haloalkylhio, C_1-C_4-haloalkylhio, C_1-C_4-haloalkylsulfinyl, C_1-C_4-haloalkylsulfonyl,}$
 - R⁹ represents C₁-C₄-haloalkyl, C₁-C₄-haloalkoxy, C₁-C₄-haloalkylsulfinyl or halogen,
 - R^{10} represents hydrogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, halogen, cyano or C_1 - C_4 -haloalkoxy,
 - in each case independently of one another represent in each case optionally monoto to trisubstituted C_1 - C_6 -alkylthio, C_1 - C_6 -alkylsulfenyl, C_1 - C_6 -haloalkythio, C_1 - C_6 -haloalkylsulfenyl, phenylthio or phenylsulfenyl, where the substituents independently of one another may be selected from the list consisting of W, $-S(O)_nN(R^{16})_2$, $-C(=O)R^{13}$, $-L(C=O)R^{14}$, $-S(C=O)LR^{14}$, $-C(=O)LR^{13}$, $-S(O)_nNR^{13}C(=O)R^{13}$, $-S(O)_nNR^{13}C(=O)LR^{14}$ and $-S(O)_nNR^{13}S(O)_2LR^{14}$,
 - L in each case independently of one another represent O, NR^{18} or S,
- 30 R^{12} in each case independently of one another represent -B(OR¹⁷)₂, amino, SH, thiocyanato, C₃-C₈-trialkylsilyloxy, C₁-C₄-alkyl disulfide, -SF₅, -C(=E)R¹⁹, -LC(=E)R¹⁹, -C(=E)LR¹⁹, -LC(=E)LR¹⁹, -OP(=Q)(OR¹⁹)₂, -SO₂LR¹⁹ or -LSO₂LR¹⁹,
 - Q represents O or S,

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in each case independently of one another represent hydrogen or represent in each case optionally mono- or polysubstituted C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl or C_3 - C_6 -cycloalkyl, where the substituents independently of one another may be selected from the

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group consisting of R^6 , halogen, cyano, nitro, hydroxyl, C_1 - C_4 -alkoxy, C_1 - C_4 -alkylsulfinyl, C_1 - C_4 -alkylsulfonyl, C_1 - C_4 -alkylamino, C_2 - C_8 -dialkylamino, C_3 - C_6 -cycloalkylamino and $(C_1$ - C_4 -alkyl) C_3 - C_6 -cycloalkylamino,

in each case independently of one another represent in each case mono- or polysubstituted C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_2 - C_{20} -alkynyl or C_3 - C_6 -cycloalkyl, where the substituents independently of one another may be selected from the group consisting of R^6 , halogen, cyano, nitro, hydroxyl, C_1 - C_4 -alkoxy, C_1 - C_4 -alkylsulfinyl, C_1 - C_4 -alkylsulfonyl, C_1 - C_4 -alkylamino, C_2 - C_8 -dialkylamino, C_3 - C_6 -cycloalkylamino and $(C_1$ - C_4 -alkyl) C_3 - C_6 -cycloalkylamino or represent optionally substituted phenyl, where the substituents independently of one another may be selected from one to three radicals R^{12} ,

in each case independently of one another represent hydrogen or represent in each case mono- or polysubstituted C₁-C₆-haloalkyl or C₁-C₆-alkyl, where the substituents independently of one another may be selected from the group consisting of cyano, nitro, hydroxyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfinyl, C₁-C₄-haloalkylsulfonyl, C₁-C₄-haloalkylsulfinyl, C₁-C₄-haloalkylsulfonyl, C₁-C₄-alkylamino, C₂-C₈-dialkylamino, C₂-C₆-alkoxycarbonyl, C₂-C₆-alkylcarbonyl, C₃-C₆-trialkylsilyl and optionally substituted phenyl, where the substituents independently of one another may be selected from one to three radicals W or one or more radicals R¹², or N(R¹⁵)₂ represents a cycle which forms the ring M,

 R^{16} represents C_1 - C_{12} -alkyl or C_1 - C_{12} -haloalkyl, or $N(R^{16})_2$ represents a cycle which forms the ring M,

R¹⁷ in each case independently of one another represent hydrogen or C₁-C₄-alkyl, or B(OR¹⁷)₂ represents a ring, where the two oxygen atoms are attached via a chain to two or three carbon atoms which are optionally substituted by one or two substituents independently of one another selected from the group consisting of methyl and C₂-C₆-alkoxycarbonyl,

 R^{18} in each case independently of one another represent hydrogen, C_1 - C_6 -alkyl or C_1 - C_6 -haloalkyl, or $N(R^{13})(R^{18})$ represents a cycle which forms the ring M,

in each case independently of one another represent hydrogen or represent in each case optionally mono- or polysubstituted C₁-C₆-alkyl, where the substituents independently of one another may be selected from the group consisting of cyano, nitro, hydroxyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-haloalkylthio, C₁-C₄-haloalkylsulfinyl, C₁-C₄-haloalkylsulfonyl, C₁-C₄-alkylamino, C₂-C₈-dialkylamino, CO₂H, C₂-C₆-alkoxycarbonyl, C₂-C₆-alkylcarbonyl, C₃-C₆-trialkylsilyl and optionally substituted phenyl, where the substituents independently of one another may be selected from one to three radicals W, C₁-C₆-haloalkyl, C₃-C₆-cycloalkyl or phenyl or

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pyridyl, each of which is optionally mono- to trisubstituted by W,

- in each case represents an optionally mono- to tetrasubstituted ring which, in addition to the nitrogen atom which is attached to the substituent pair R^{13} and R^{18} , $(R^{15})_2$ or $(R^{16})_2$, contains two to six carbon atoms and optionally additionally a further nitrogen, sulfur or oxygen atom, and where the substituents independently of one another may be selected from the group consisting of C_1 - C_2 -alkyl, halogen, cyano, nitro and C_1 - C_2 -alkoxy,
- in each case independently of one another represent C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₃-C₆-cycloalkyl, C₁-C₄-haloalkyl, C₂-C₄-haloalkenyl, C₂-C₄-haloalkynyl, C₃-C₆-halocycloalkyl, halogen, cyano, nitro, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-alkylamino, C₂-C₈-dialkylamino, C₃-C₆-cycloalkylamino, (C₁-C₄-alkyl)C₃-C₆-cycloalkylamino, C₂-C₄-alkylcarbonyl, C₂-C₆-alkoxy-carbonyl, C₂-C₆-alkylaminocarbonyl, C₃-C₈-dialkylaminocarbonyl or C₃-C₆-trialkylsilyl,
- n in each case independently of one another represent 0 or 1,
- 15 p in each case independently of one another represent 0, 1 or 2,

where in the case that (a) R⁵ represents hydrogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₂-C₆-haloalkenyl, C₂-C₆-haloalkynyl, C₁-C₄-haloalkoxy, C₁-C₄-haloalkylthio or halogen and (b) R⁸ represents hydrogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₂-C₆-haloalkynyl, C₁-C₄-haloalkoxy, C₁-C₄-haloalkyl, C₂-C₆-haloalkynyl, C₁-C₄-haloalkoxy, C₁-C₄-haloalkylthio, halogen, C₂-C₄-alkylcarbonyl, C₂-C₆-alkoxycarbonyl, C₂-C₆-alkylaminocarbonyl or C₃-C₈ dialkylaminocarbonyl, (c) at least one substituent selected from the group consisting of R⁶, R¹¹ and R¹² is present and (d), if R¹² is not present, at least one R⁶ or R¹¹ is different from C₂-C₆-alkylcarbonyl, C₂-C₆ alkoxycarbonyl, C₂-C₆-alkylaminocarbonyl and C₃-C₈-dialkylaminocarbonyl, and

25 the compounds of the general formula (I) also include N-oxides and salts,

and at least one active compound from the group of the pyrethroids (active compounds of group 2) is synergistically effective and suitable for controlling animal pests.

Depending inter alia on the nature of the substituents, the compounds of the formula (I) may be present as geometrical and/or optical isomers or isomer mixtures of varying composition which, if appropriate, may be separated in a customary manner. The present invention provides both the pure isomers and the isomer mixtures, their preparation and use and also compositions comprising them. However, hereinbelow, for the sake of simplicity, only compounds of the formula (I) are referred to, although what is meant are both the pure compounds and, if appropriate, also mixtures having varying proportions of isomeric compounds.

Preference is given to active compound combinations comprising compounds of the formula (I-1)

$$\mathbb{R}^{5}$$
 \mathbb{R}^{4}
 \mathbb{R}^{9}
 \mathbb{R}^{9}
 \mathbb{R}^{2}
 \mathbb{R}^{2}
 \mathbb{R}^{2}
 \mathbb{R}^{2}
 \mathbb{R}^{3}
 \mathbb{R}^{4}
 \mathbb{R}^{4}
 \mathbb{R}^{9}
 \mathbb{R}^{9}
 \mathbb{R}^{9}

5 in which

R² represents hydrogen or C₁-C₆-alkyl,

R³ represents C₁-C₆-alkyl which is optionally substituted by a radical R⁶,

R⁴ represents C₁-C₄-alkyl, C₁-C₂-haloalkyl, C₁-C₂-haloalkoxy or halogen,

R⁵ represents hydrogen, C₁-C₄-alkyl, C₁-C₂-haloalkyl, C₁-C₂-haloalkoxy or halogen,

10 R⁶ represents -C(=E²)R¹⁹, -LC(=E²)R¹⁹, -C(=E²)LR¹⁹ or -LC(=E²)LR¹⁹, where each E² independently of the others represents O, S, N-R¹⁵, N-OR¹⁵, N-N(R¹⁵)₂, and each L independently of the others represents O or NR¹⁸,

R⁷ represents C₁-C₄-haloalkyl or halogen,

R⁸ represents hydrogen,

15 R^9 represents C_1 - C_2 -haloalkyl, C_1 - C_2 -haloalkoxy, $S(O)_pC_1$ - C_2 -haloalkyl or halogen,

 $R^{15} \qquad \text{in each case independently of one another represent hydrogen or represent in each case} \\ \text{optionally substituted C_1-C_6-haloalkyl or C_1-C_6-alkyl, where the substituent independently} \\ \text{of one another may be selected from the group consisting of cyano, C_1-C_4-alkoxy, C_1-C_4-haloalkylthio, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, C_1-C_4-haloalkylthio,} \\ \text{haloalkoxy, C_1-C_4-alkylthio, C_1-C_4-alkylsulfonyl, C_1-C_4-haloalkylthio,} \\ \text{haloalkoxy, C_1-C_4-alkylthio,} \\ \text{hal$

20 C₁-C₄-haloalkylsulfinyl or C₁-C₄-haloalkylsulfonyl,

 R^{18} in each case represents hydrogen or C_1 - C_4 -alkyl,

R¹⁹ in each case independently of one another represent hydrogen or C₁-C₆-alkyl,

p independently of one another represents 0, 1, 2.

In the radical definitions mentioned as being preferred, halogen represents fluorine, chlorine, bromine and iodine, in particular fluorine, chlorine and bromine.

Particular preference is given to active compound combinations comprising compounds of the formula (I-1), in which

30 R² represents hydrogen or methyl,

 R^3 represents C_1 - C_4 -alkyl,

R⁴ represents methyl, trifluoromethyl, trifluoromethoxy, fluorine, chlorine, bromine or iodine,

R⁵ represents hydrogen, fluorine, chlorine, bromine, iodine, trifluoromethyl or trifluoromethoxy,

R⁷ represents chlorine or bromine,

R⁸ represents hydrogen,

5 R⁹ represents trifluoromethyl, chlorine, bromine, difluoromethoxy or trifluoroethoxy.

Very particular preference is given to active compound combinations comprising the following compounds of the formula (I-1):

$$R^3$$
 N N N N R^7 R^4 O N N R^8

Example No.	R ²	R ³	R ⁴	R ⁵	\mathbb{R}^7	R ⁹	m.p. (°C)
I-1-1	Н	Me	Me	Cl	Cl	CF ₃	185-186
I-1-2	H	Me	Me	Cl	Cl	OCH ₂ CF ₃	207-208
I-1-3	H	Me	Me	Cl	Cl	C1	225-226
I-1-4	H	Me	Me	Cl	Cl	Br	162-164
I-1-5	H	Me	Cl	Cl	C1	CF_3	155-157
I-1-6	H	Me	C1	Cl	C1	OCH ₂ CF ₃	192-195
I- 1-7	\mathbf{H}	Me	Cl	C1	C1	Cl	205-206
I-1-8	H	Me	C1	Cl	Cl	Br	245-246
I-1-9	H	i-Pr	Me	C1	Cl	CF_3	195-196
I-1-10	H	i-Pr	Me	Cl	Cl	OCH ₂ CF ₃	217-218
I-1-11	H	i-Pr	Me	Cl	C1	Cl	173-175
I-1-12	Н	i-Pr	Me	Cl	C1	Br	159-161
I-1-13	Н	i-Pr	Cl	Cl	C1	CF ₃	200-201
I-1-14	H	i-Pr	Cl	Cl	C1	OCH ₂ CF ₃	232-235
I-1-15	H	i-Pr	Cl	Cl	Cl	Cl	197-199
I-1-16	H	i-Pr	Cl	C1	C1	Br	188-190

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Especially preferred are active compound combinations comprising the active compound of the formula (I-1-9)

$$H_3C$$
 H_3C
 H_3C
 N
 N
 CI
 CF_3
 CF_3

Especially preferred are active compound combinations comprising the active compound of the formula (I-1-11)

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Especially preferred are active compound combinations comprising the active compound of the formula (I-1-12)

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Pyrethroids are known active compounds having insecticidal and acaricidal properties. Preference is given to active compound combinations according to the invention which, preferably, comprise the following pyrethroids (active compounds of group 2):

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(2-1) acrinathrin (known from EP-A 0 048 186)

(2-2) alpha-cypermethrin (known from EP-A 0 067 461)

and/or

5 (2-3) betacyfluthrin (known from EP-A 0 206 149)

and/or

(2-4) cyhalothrin (known from DE-A 28 02 962)

10 and/or

(2-5) cypermethrin (known from DE-A-2 326 077)

and/or

(2-6) deltamethrin (known from DE-A 23 26 077)

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and/or

(2-7) esfenvalerate (known from DE-A 27 37 297)

(2-8) ethofenprox (known from DE-A 31 17 510)

$$\mathsf{H_{5}C_{2}O} \underbrace{\mathsf{O}}_{\mathsf{H_{3}C}} \mathsf{CH_{3}}$$

and/or

5 (2-9) fenpropathrin (known from DE-A 22 31 312)

$$H_3C$$
 CH_3
 CH_3

and/or

(2-10) fenvalerate (known from DE-A 23 35 347)

10 and/or

(2-11) flucythrinate (known from DE-A 27 57 066)

and/or

(2-12) lambda-cyhalothrin (known from EP-A 0 106 469)

15 and/or

(2-13) permethrin (known from DE-A 23 26 077)

and/or

20 (2-14) taufluvalinate (known from EP-A 0 038 617)

(2-15) tralomethrin (known from DE-A 27 42 546)

5 and/or

(2-16) zeta-cypermethrin (known from EP-A 0 026 542)

and/or

(2-17) cyfluthrin (known from DE-A 27 09 264)

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and/or

(2-18) bifenthrin (known from EP-A 0 049 977)

and/or

15 (2-19) cycloprothrin (known from DE-A 26 53 189)

and/or

(2-20) eflusilanate (known from DE-A 36 04 781)

(2-21) fubfenprox (known from DE-A 37 08 231)

5 and/or

(2-22) pyrethrin (known from The Pesticide Manual, 1997, 11th edition, p. 1056)

$$R^{20} \xrightarrow{H_3C} CH_3 \xrightarrow{H_3C} CH_2 \xrightarrow{H} R^{21}$$

 $R^{20} = -CH_3 \text{ or } -CO_2CH_3$

 $R^{21} = -CH = CH_2 \text{ or } -CH_3 \text{ or } -CH_2CH_3$

10 and/or

(2-23) resmethrin (known from GB-A 1 168 797)

and/or

(2-24) gamma-cyhalothrin (known from GB-A 2 143 823)

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Particularly preferably, the active compound combinations according to the invention comprise at least one pyrethroid of group 2 selected from

- (2-3) betacyfluthrin.
- 20 (2-5) cypermethrin.
 - (2-6) deltamethrin.
 - (2-12) lambda-cyhalothrin.
 - (2-14) taufluvalinate.
 - (2-24) gamma-cyhalothrin.

Especially preferred are active compound combinations comprising the compound of the formula (I-1-9) and a pyrethroid of group 2 selected from the compounds (2-1) to (2-24).

Especially preferred are active compound combinations comprising the compound of the formula 5 (I-1-11) and a pyrethroid of group 2 selected from the compounds (2-1) to (2-24).

Especially preferred are active compound combinations comprising the compound of the formula (I-1-12) and a pyrethroid of group 2 selected from the compounds (2-1) to (2-24).

- Emphasis is given to the following active compound combinations comprising the compound of the formula (I-1-9) and the given pyrethroid of group 2:
 - a) Active compound combination comprising (I-1-9) and (2-1) acrinathrin.
 - b) Active compound combination comprising (I-1-9) and (2-3) betacyfluthrin.
- 15 c) Active compound combination comprising (I-1-9) and (2-5) cypermethrin.
 - d) Active compound combination comprising (I-1-9) and (2-6) deltamethrin.
 - e) Active compound combination comprising (I-1-9) and (2-12) lambda-cyhalothrin.
 - f) Active compound combination comprising (I-1-9) and (2-14) taufluvalinate.
 - g) Active compound combination comprising (I-1-9) and (2-24) gamma-cyhalothrin.

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Emphasis is given to the following active compound combinations comprising the compound of the formula (I-1-11) and the given pyrethroid of group 2:

- h) Active compound combination comprising (I-1-11) and (2-1) acrinathrin.
- i) Active compound combination comprising (I-1-11) and (2-3) betacyfluthrin.
- 25 k) Active compound combination comprising (I-1-11) and (2-5) cypermethrin.
 - 1) Active compound combination comprising (I-1-11) and (2-6) deltamethrin.
 - m) Active compound combination comprising (I-1-11) and (2-12) lambda-cyhalothrin.
 - n) Active compound combination comprising (I-1-11) and (2-14) taufluvalinate.
 - o) Active compound combination comprising (I-1-11) and (2-24) gamma-cyhalothrin.

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Emphasis is given to the following active compound combinations comprising the compound of the formula (I-1-12) and the given pyrethroid of group 2:

- p) Active compound combination comprising (I-1-12) and (2-1) acrinathrin.
- q) Active compound combination comprising (I-1-12) and (2-3) betacyfluthrin.
- 35 r) Active compound combination comprising (I-1-12) and (2-5) cypermethrin.
 - w) Active compound combination comprising (I-1-12) and (2-6) deltamethrin.

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- t) Active compound combination comprising (I-1-12) and(2-12) lambda-cyhalothrin.
- u) Active compound combination comprising (I-1-12) and (2-14) taufluvalinate.
- v) Active compound combination comprising (I-1-12) and (2-24) gamma-cyhalothrin.
- However, the general or preferred radical definitions or illustrations listed above can also be combined with one another as desired, i.e. between their respective ranges and preferred ranges. The definitions apply to the end products and, correspondingly, to precursors and intermediates.
- Preference according to the invention is given to active compound combinations comprising compounds of the formula (I) and pyrethroids of the formulae (2-1) to (2-24), where the individual radicals are a combination of the meanings listed above as being preferred (preferable).

Particular preference according to the invention is given to active compound combinations comprising compounds of the formula (I) and pyrethroids of the formulae (2-1) to (2-24), where the individual radicals are a combination of the meanings listed above as being particularly preferred.

Very particular preference according to the invention is given to active compound combinations comprising compounds of the formula (I) and pyrethroids of the formulae (2-1) to (2-24), where the individual radicals are a combination of the meanings listed above as being very particularly preferred.

Saturated or unsaturated hydrocarbon radicals, such as alkyl or alkenyl, can in each case be straightchain or branched as far as this is possible, including in combination with heteroatoms, such as, for example, in alkoxy.

Optionally substituted radicals can be mono- or polysubstituted, where in the case of polysubstitution the substituents can be identical or different.

In addition, the active compound combinations may also comprise further fungicidally, acaricidally or insecticidally active additives.

If the active compounds in the active compound combinations according to the invention are present in certain weight ratios, the synergistic effect is particularly pronounced. However, the weight ratios of the active compounds in the active compound combinations can be varied within a relatively wide range. In general, the combinations according to the invention comprise active compounds of the

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formula (I) and the mixing partner of the group 2 in the preferred and particularly preferred mixing ratios given:

* the mixing ratios are based on weight ratios. The ratio is to be understood as meaning active compound of the formula (I):mixing partner

Mixing partner	Preferred mixing ratio	Particularly preferred mixing ratio
Acrinathrin	20:1 to 1:50	10:1 to 1:1
Alpha-Cypermethrin	50:1 to 1:5	10:1 to 1:1
Betacyfluthrin	50:1 to 1:5	10:1 to 1:1
cyhalothrin	50:1 to 1:5	10:1 to 1:1
cypermethrin	50:1 to 1:5	10:1 to 1:1
deltamethrin	50:1 to 1:5	10:1 to 1:1
esfenvalerate	50:1 to 1:5	10:1 to 1:1
etofenprox	10:1 to 1:10	5:1 to 1:5
fenpropathrin	10:1 to 1:10	5:1 to 1:5
fenvalerate	20:1 to 1:5	10:1 to 1:1
flucythrinate	50:1 to 1:5	10:1 to 1:1
lambda-cyhalothrin	50:1 to 1:5	10:1 to 1:1
permethrin	10:1 to 1:10	5:1 to 1:5
tau-fluvalinate	20:1 to 1:5	10:1 to 1:2
tralomethrin	50:1 to 1:5	10:1 to 1:1
zeta-cypermethrin	50:1 to 1:5	10:1 to 1:2
cyfluthrin	50:1 to 1:5	10:1 to 1:1
bifenthrin	10:1 to 1:10	10:1 to 1:1
cycloprothrin	10:1 to 1:10	5:1 to 1:5
eflusilanate	10:1 to 1:10	5:1 to 1:5
fubfenprox	10:1 to 1:10	5:1 to 1:5
pyrethrin	50:1 to 1:10	5:1 to 1:1
resmethrin	50:1 to 1:10	5:1 to 1:1
gamma-cyhalothrin	50:1 to 1:5	10:1 to 1:1

The active compound combinations according to the invention are suitable for controlling animal pests, preferably arthropods and nematodes, in particular insects and arachnids, found in agriculture, in animal health, in forests, in the protection of stored products and materials and in the hygiene

sector. They are active against normally sensitive and resistant species, and against all or individual developmental stages. The abovementioned pests include:

From the order of the Isopoda, for example, Oniscus asellus, Armadillidium vulgare, Porcellio scaber.

From the order of the Diplopoda, for example, Blaniulus guttulatus.

From the order of the Chilopoda, for example, Geophilus carpophagus, Scutigera spp.

From the order of the Symphyla, for example, Scutigerella immaculata.

From the order of the Thysanura, for example, Lepisma saccharina.

From the order of the Collembola, for example, Onychiurus armatus.

10 From the order of the Orthoptera, for example, Acheta domesticus, Gryllotalpa spp., Locusta migratoria migratorioides, Melanoplus spp., Schistocerca gregaria.

From the order of the Blattaria, for example, Blatta orientalis, Periplaneta americana, Leucophaea maderae, Blattella germanica.

From the order of the Dermaptera, for example, Forficula auricularia.

15 From the order of the Isoptera, for example, Reticulitermes spp.

From the order of the Phthiraptera, for example, Pediculus humanus corporis, Haematopinus spp., Linognathus spp., Trichodectes spp., Damalinia spp.

From the order of the Thysanoptera, for example, Hercinothrips femoralis, Thrips tabaci, Thrips palmi, Frankliniella occidentalis.

From the order of the Heteroptera, for example, Eurygaster spp., Dysdercus intermedius, Piesma quadrata, Cimex lectularius, Rhodnius prolixus, Triatoma spp.

From the order of the Homoptera, for example, Aleurodes brassicae, Bemisia tabaci, Trialeurodes vaporariorum, Aphis gossypii, Brevicoryne brassicae, Cryptomyzus ribis, Aphis fabae, Aphis pomi, Eriosoma lanigerum, Hyalopterus arundinis, Phylloxera vastatrix, Pemphigus spp., Macrosiphum avenae, Myzus spp., Phorodon humuli, Rhopalosiphum padi, Empoasca spp., Euscelis bilobatus, Nephotettix cincticeps, Lecanium corni, Saissetia oleae, Laodelphax striatellus, Nilaparvata lugens,

Aonidiella aurantii, Aspidiotus hederae, Pseudococcus spp., Psylla spp.

From the order of the Lepidoptera, for example, Pectinophora gossypiella, Bupalus piniarius, Cheimatobia brumata, Lithocolletis blancardella, Hyponomeuta padella, Plutella xylostella,

- Malacosoma neustria, Euproctis chrysorrhoea, Lymantria spp., Bucculatrix thurberiella, Phyllocnistis citrella, Agrotis spp., Euxoa spp., Feltia spp., Earias insulana, Heliothis spp., Mamestra brassicae, Panolis flammea, Spodoptera spp., Trichoplusia ni, Carpocapsa pomonella, Pieris spp., Chilo spp., Pyrausta nubilalis, Ephestia kuehniella, Galleria mellonella, Tineola bisselliella, Tinea pellionella, Hofmannophila pseudospretella, Cacoecia podana, Capua reticulana, Choristoneura fumiferana,
- 35 Clysia ambiguella, Homona magnanima, Tortrix viridana, Cnaphalocerus spp., Oulema oryzae.

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From the order of the Coleoptera, for example, Anobium punctatum, Rhizopertha dominica, Bruchidius obtectus, Acanthoscelides obtectus, Hylotrupes bajulus, Agelastica alni, Leptinotarsa decemlineata, Phaedon cochleariae, Diabrotica spp., Psylliodes chrysocephala, Epilachna varivestis, Atomaria spp., Oryzaephilus surinamensis, Anthonomus spp., Sitophilus spp., Otiorrhynchus sulcatus, Cosmopolites sordidus, Ceuthorrhynchus assimilis, Hypera postica, Dermestes spp., Trogoderma spp., Anthrenus spp., Attagenus spp., Lyctus spp., Meligethes aeneus, Ptinus spp., Niptus hololeucus, Gibbium psylloides, Tribolium spp., Tenebrio molitor, Agriotes spp., Conoderus spp., Melolontha melolontha, Amphimallon solstitialis, Costelytra zealandica, Lissorhoptrus oryzophilus.

From the order of the Hymenoptera, for example, Diprion spp., Hoplocampa spp., Lasius spp., Monomorium pharaonis, Vespa spp.

From the order of the Diptera, for example, Aedes spp., Anopheles spp., Culex spp., Drosophila melanogaster, Musca spp., Fannia spp., Calliphora erythrocephala, Lucilia spp., Chrysomyia spp., Cuterebra spp., Gastrophilus spp., Hyppobosca spp., Stomoxys spp., Oestrus spp., Hypoderma spp.,

Tabanus spp., Tannia spp., Bibio hortulanus, Oscinella frit, Phorbia spp., Pegomyia hyoscyami, Ceratitis capitata, Dacus oleae, Tipula paludosa, Hylemyia spp., Liriomyza spp.

From the order of the Siphonaptera, for example, Xenopsylla cheopis, Ceratophyllus spp.

From the class of the Arachnida, for example, Scorpio maurus, Latrodectus mactans, Acarus siro, Argas spp., Ornithodoros spp., Dermanyssus gallinae, Eriophyes ribis, Phyllocoptruta oleivora,

Boophilus spp., Rhipicephalus spp., Amblyomma spp., Hyalomma spp., Ixodes spp., Psoroptes spp., Chorioptes spp., Sarcoptes spp., Tarsonemus spp., Bryobia praetiosa, Panonychus spp., Tetranychus spp., Hemitarsonemus spp., Brevipalpus spp.

The plant-parasitic nematodes include, for example, Pratylenchus spp., Radopholus similis,

Ditylenchus dipsaci, Tylenchulus semipenetrans, Heterodera spp., Globodera spp., Meloidogyne spp.,

Aphelenchoides spp., Longidorus spp., Xiphinema spp., Trichodorus spp., Bursaphelenchus spp.

The active compound combinations can be converted into the customary formulations such as solutions, emulsions, wettable powders, suspensions, powders, dusts, pastes, soluble powders, granules, suspension-emulsion concentrates, natural and synthetic materials impregnated with active compound, and microencapsulations in polymeric materials.

These formulations are produced in a known manner, for example by mixing the active compounds with extenders, that is, liquid solvents and/or solid carriers, optionally with the use of surfactants, that is, emulsifiers and/or dispersants, and/or foam formers.

If the extender used is water, it is also possible, for example, to use organic solvents as cosolvents. The following are essentially suitable as liquid solvents: aromatics such as xylene, toluene or alkylnaphthalenes, chlorinated aromatics or chlorinated aliphatic hydrocarbons such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons such as cyclohexane or paraffins, for example mineral oil fractions, mineral and vegetable oils, alcohols such as butanol or glycol and their ethers and esters, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents such as dimethylformamide and dimethyl sulfoxide, or else water.

10 Suitable solid carriers are:

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for example ammonium salts and ground natural minerals such as kaolins, clays, tale, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic materials such as highly disperse silica, alumina and silicates; suitable solid carriers for granules are: for example crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, or else synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, corn cobs and tobacco stalks; suitable emulsifiers and/or foam formers are: for example nonionic and anionic emulsifiers such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulfonates, alkyl sulfates, arylsulfonates, or else protein hydrolysates; suitable dispersants are: for example lignosulfite waste liquors and methylcellulose.

Tackifiers such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, or else natural phospholipids such as cephalins and lecithins and synthetic phospholipids can be used in the formulations. Other possible additives are mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic colorants such as alizarin colorants, azo colorants and metal phthalocyanine colorants, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations generally comprise between 0.1 and 95% by weight of active compound, preferably between 0.5 and 90%.

The active compound combinations according to the invention can be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with

other active compounds, such as insecticides, attractants, sterilants, bactericides, acaricides, nematicides, fungicides, growth-regulating substances or herbicides. The insecticides include, for example, phosphates, carbamates, carboxylates, chlorinated hydrocarbons, phenylureas and substances produced by microorganisms, inter alia.

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Mixtures with other known active compounds such as herbicides or with fertilizers and growth regulators are also possible.

When used as insecticides, the active compound combinations according to the invention can furthermore be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with synergists. Synergists are compounds which increase the action of the active compounds, without it being necessary for the synergist added to be active itself.

The active compound content of the use forms prepared from the commercially available formulations can vary within wide limits. The active compound concentration of the use forms can be from 0.0000001 to 95% by weight of active compound, preferably between 0.0001 and 1% by weight.

The compounds are employed in a customary manner appropriate for the use forms.

When used against hygiene pests and stored-product pests, the active compound combinations are distinguished by an excellent residual action on wood and clay as well as good stability to alkali on limed substrates.

The active compound combinations according to the invention are not only active against plant pests, hygiene pests and stored-product pests, but also, in the veterinary medicine sector, against animal parasites (ectoparasites) such as hard ticks, soft ticks, mange mites, harvest mites, flies (stinging and licking), parasitizing fly larvae, lice, head lice, bird lice and fleas. These parasites include:

From the order of the Anoplurida, for example, Haematopinus spp., Linognathus spp., Pediculus spp., Phtirus spp., Solenopotes spp.

From the order of the Mallophagida and the suborders Amblycerina and Ischnocerina, for example,

Trimenopon spp., Menopon spp., Trinoton spp., Bovicola spp., Werneckiella spp., Lepikentron spp.,

Damalina spp., Trichodectes spp., Felicola spp.

From the order Diptera and the suborders Nematocerina and Brachycerina, for example, Aedes spp., Anopheles spp., Culex spp., Simulium spp., Eusimulium spp., Phlebotomus spp., Lutzomyia spp., Culicoides spp., Chrysops spp., Hybomitra spp., Atylotus spp., Tabanus spp., Haematopota spp.,

35 Philipomyia spp., Braula spp., Musca spp., Hydrotaea spp., Stomoxys spp., Haematobia spp.,

Morellia spp., Fannia spp., Glossina spp., Calliphora spp., Lucilia spp., Chrysomyia spp., Wohlfahrtia spp., Sarcophaga spp., Oestrus spp., Hypoderma spp., Gasterophilus spp., Hippobosca spp., Lipoptena spp., Melophagus spp.

From the order of the Siphonapterida, for example, Pulex spp., Ctenocephalides spp., Xenopsylla spp., Ceratophyllus spp.

From the order of the Heteropterida, for example, Cimex spp., Triatoma spp., Rhodnius spp., Panstrongylus spp.

From the order of the Blattarida, for example, Blatta orientalis, Periplaneta americana, Blattella germanica, Supella spp.

From the subclass of the Acaria (Acarida) and the orders of the Meta- and Mesostigmata, for example, Argas spp., Ornithodorus spp., Otobius spp., Ixodes spp., Amblyomma spp., Boophilus spp., Dermacentor spp., Haemophysalis spp., Hyalomma spp., Rhipicephalus spp., Dermanyssus spp., Raillietia spp., Pneumonyssus spp., Sternostoma spp., Varroa spp.

From the order of the Actinedida (Prostigmata) and Acaridida (Astigmata), for example, Acarapis spp., Cheyletiella spp., Ornithocheyletia spp., Myobia spp., Psorergates spp., Demodex spp., Trombicula spp., Listrophorus spp., Acarus spp., Tyrophagus spp., Caloglyphus spp., Hypodectes spp., Pterolichus spp., Psoroptes spp., Chorioptes spp., Otodectes spp., Sarcoptes spp., Notoedres spp., Knemidocoptes spp., Cytodites spp., Laminosioptes spp.

The active compound combinations according to the invention are also suitable for controlling arthropods which attack agricultural livestock such as, for example, cattle, sheep, goats, horses, pigs, donkeys, camels, buffaloes, rabbits, chickens, turkeys, ducks, geese, honey-bees, other domestic animals such as, for example, dogs, cats, caged birds, aquarium fish and so-called experimental animals such as, for example, hamsters, guinea pigs, rats and mice. By controlling these arthropods, cases of death and reductions in productivity (for meat, milk, wool, hides, eggs, honey and the like) should be diminished, so that more economical and simpler animal husbandry is possible by the use of the active compound combinations according to the invention.

The active compound combinations according to the invention are used in the veterinary sector in a known manner by enteral administration in the form of, for example, tablets, capsules, potions, drenches, granules, pastes, boluses, the feed-through method, suppositories, by parenteral administration such as, for example, by injections (intramuscularly, subcutaneously, intravenously, intraperitoneally and the like), implants, by nasal administration, by dermal administration in the form of, for example, immersing or dipping, spraying, pouring-on, spotting-on, washing, dusting, and with the aid of active-compound-comprising molded articles such as collars, ear tags, tail tags, limb bands, halters, marking devices and the like.

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When used for cattle, poultry, domestic animals and the like, the active compound combinations can be applied as formulations (for example powders, emulsions, flowables) comprising the active compounds in an amount of 1 to 80% by weight, either directly or after 100- to 10 000-fold dilution, or they may be used as a chemical dip.

Moreover, it has been found that the active compound combinations according to the invention show a potent insecticidal action against insects which destroy industrial materials.

The following insects may be mentioned by way of example and with preference, but not by way of limitation:

Beetles such as Hylotrupes bajulus, Chlorophorus pilosis, Anobium punctatum, Xestobium rufovillosum, Ptilinus pecticornis, Dendrobium pertinex, Ernobius mollis, Priobium carpini, Lyctus brunneus, Lyctus africanus, Lyctus planicollis, Lyctus linearis, Lyctus pubescens, Trogoxylon aequale, Minthes rugicollis, Xyleborus spec., Tryptodendron spec., Apate monachus, Bostrychus capucins, Heterobostrychus brunneus, Sinoxylon spec., Dinoderus minutus.

Dermapterans such as Sirex juvencus, Urocerus gigas, Urocerus gigas taignus, Urocerus augur.

Termites such as Kalotermes flavicollis, Cryptotermes brevis, Heterotermes indicola, Reticulitermes flavipes, Reticulitermes santonensis, Reticulitermes lucifugus, Mastotermes darwiniensis, Zootermopsis nevadensis, Coptotermes formosanus.

20 Bristle-tails such as Lepisma saccharina.

Industrial materials in the present context are understood as meaning non-living materials such as, preferably, polymers, adhesives, glues, paper and board, leather, wood, timber products and paints.

The material which is to be protected from insect attack is very particularly preferably wood and timber products.

Wood and timber products which can be protected by the composition according to the invention, or mixtures comprising it, are to be understood as meaning, for example:

30 Construction timber, wooden beams, railway sleepers, bridge components, jetties, vehicles made of wood, boxes, pallets, containers, telephone poles, wood lagging, windows and doors made of wood, plywood, chipboard, joinery, or timber products which quite generally are used in house construction or building joinery.

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The active compound combinations can be used as such, in the form of concentrates or generally customary formulations such as powders, granules, solutions, suspensions, emulsions or pastes.

The abovementioned formulations can be prepared in a manner known per se, for example by mixing the active compounds with at least one solvent or diluent, emulsifier, dispersant and/or binder or fixative, water repellant, if desired desiccants and UV stabilizers, and if desired colorants and pigments and other processing auxiliaries.

The insecticidal compositions or concentrates used for protecting wood and timber products comprise the active compound according to the invention in a concentration of 0.0001 to 95% by weight, in particular 0.001 to 60% by weight.

The amount of composition or concentrate employed depends on the species and the abundance of the insects and on the medium. The optimal quantity to be employed can be determined in each case by test series upon application. In general, however, it will suffice to employ 0.0001 to 20% by weight, preferably 0.001 to 10% by weight, of the active compound, based on the material to be protected.

A suitable solvent and/or diluent is an organochemical solvent or solvent mixture and/or an oily or oil-type organochemical solvent or solvent mixture of low volatility and/or a polar organochemical solvent or solvent mixture and/or water and, if appropriate, an emulsifier and/or wetter.

Organochemical solvents which are preferably employed are oily or oil-type solvents with an evaporation number of above 35 and a flash point of above 30°C, preferably above 45°C. Such oily and oil-type solvents which are insoluble in water and of low volatility and which are used are suitable mineral oils or their aromatic fractions or mineral-oil-containing solvent mixtures, preferably white spirit, petroleum and/or alkylbenzene.

Mineral oils with a boiling range of 170 to 220°C, white spirit with a boiling range of 170 to 220°C, spindle oil with a boiling range of 250 to 350°C, petroleum and aromatics with a boiling range of 160 to 280°C, oil of turpentine, and the like are advantageously used.

In a preferred embodiment, liquid aliphatic hydrocarbons with a boiling range of 180 to 210°C or high-boiling mixtures of aromatic and aliphatic hydrocarbons with a boiling range of 180 to 220°C and/or spindle oil and/or monochloronaphthalene, preferably α-monochloronaphthalene, are used.

The organic oily or oil-type solvents of low volatility and with an evaporation number of above 35 and a flash point of above 30°C, preferably above 45°C, can be replaced in part by organochemical solvents of high or medium volatility, with the proviso that the solvent mixture also has an evaporation number of above 35 and a flash point of above 30°C, preferably above 45°C, and that the mixture is soluble or emulsifiable in this solvent mixture.

In a preferred embodiment, some of the organochemical solvent or solvent mixture or an aliphatic polar organochemical solvent or solvent mixture is replaced. Aliphatic organochemical solvents which contain hydroxyl and/or ester and/or ether groups are preferably used, such as, for example, glycol ethers, esters or the like.

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Organochemical binders used for the purposes of the present invention are the synthetic resins and/or binding drying oils which are known per se and which can be diluted in water and/or dissolved or dispersed or emulsified in the organochemical solvents employed, in particular binders composed of, or comprising, an acrylate resin, a vinyl resin, for example polyvinyl acetate, polyester resin, polycondensation or polyaddition resin, polyurethane resin, alkyd resin or modified alkyd resin, phenol resin, hydrocarbon resin such as indene/coumarone resin, silicone resin, drying vegetable and/or drying oils and/or physically drying binders based on a natural and/or synthetic resin.

The synthetic resin employed as binder can be employed in the form of an emulsion, dispersion or solution. Bitumen or bituminous substances may also be used as binders, in amounts of up to 10% by weight. In addition, colorants, pigments, water repellants, odor-masking agents, and inhibitors or anticorrosive agents and the like, all of which are known per se, can be employed.

In accordance with the invention, the composition or the concentrate preferably comprises, as organochemical binders, at least one alkyd resin or modified alkyd resin and/or a drying vegetable oil. Alkyd resins which are preferably used in accordance with the invention are those with an oil content of over 45% by weight, preferably 50 to 68% by weight.

Some or all of the abovementioned binder can be replaced by a fixative (mixture) or plasticizer (mixture). These additives are intended to prevent volatilization of the active compounds, and also crystallization or precipitation. They preferably replace 0.01 to 30% of the binder (based on 100% of binder employed).

The plasticizers are from the chemical classes of the phthalic esters, such as dibutyl phthalate, dioctyl phthalate or benzyl butyl phthalate, phosphoric esters such as tributyl phosphate, adipic esters such as

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di(2-ethylhexyl) adipate, stearates such as butyl stearate or amyl stearate, oleates such as butyl oleate, glycerol ethers or higher-molecular-weight glycol ethers, glycerol esters and p-toluenesulfonic esters.

Fixatives are based chemically on polyvinyl alkyl ethers such as, for example, polyvinyl methyl ether, or ketones such as benzophenone and ethylenebenzophenone.

Other suitable solvents or diluents are, in particular, water, if appropriate as a mixture with one or more of the abovementioned organochemical solvents or diluents, emulsifiers and dispersants.

Particularly effective timber protection is achieved by industrial-scale impregnating processes, for example the vacuum, double-vacuum or pressure processes.

The active compound combinations according to the invention can equally be employed for protecting objects which come into contact with saltwater or brackish water, in particular hulls, screens, nets, buildings, quaysides and signaling systems, against fouling.

Fouling by sessile Oligochaeta, such as Serpulidae, and by shells and species from the Ledamorpha group (goose barnacles), such as various Lepas and Scalpellum species, or by species from the Balanomorpha group (acorn barnacles), such as Balanus or Pollicipes species, increases the frictional drag of ships and, as a consequence, leads to a marked increase in operation costs owing to higher energy consumption and additionally frequent stops in the dry dock.

Apart from fouling by algae, for example Ectocarpus sp. and Ceramium sp., in particular fouling by sessile Entomostraka groups, which come under the generic term Cirripedia (cirriped crustaceans), is of particular importance.

Surprisingly, it has now been found that the active compound combinations according to the invention have an outstanding antifouling action.

30 Use of the active compound combinations according to the invention allows the use of heavy metals such as, for example, in bis(trialkyltin) sulfides, tri-*n*-butyltin laurate, tri-*n*-butyltin chloride, copper(I) oxide, triethyltin chloride, tri-*n*-butyl(2-phenyl-4-chlorophenoxy)tin, tributyltin oxide, molybdenum disulfide, antimony oxide, polymeric butyl titanate, phenyl (bispyridine)bismuth chloride, tri-*n*-butyltin fluoride, manganese ethylenebisthiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisthiocarbamate, zinc salts and copper salts of 2-pyridinethiol 1-oxide, bisdimethyldithiocarbamoylzinc ethylenebisthiocarbamate, zinc oxide, copper(I) ethylenebisdithiocarbamate,

copper thiocyanate, copper naphthenate and tributyltin halides to be dispensed with, or the concentration of these compounds to be substantially reduced.

If appropriate, the ready-to-use antifouling paints can additionally comprise other active compounds, preferably algicides, fungicides, herbicides, molluscicides, or other antifouling active compounds.

Preferable suitable combination partners for the antifouling compositions according to the invention are:

algicides such as 2-*tert*-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine, dichlorophen, diuron, endothal, fentin acetate, isoproturon, methabenzthiazuron, oxyfluorfen, quinoclamine and terbutryn;

fungicides such as benzo[b]thiophenecarboxylic acid cyclohexylamide S,S-dioxide, dichlofluanid, fluorfolpet, 3-iodo-2-propynyl butylcarbamate, tolylfluanid and azoles such as azaconazole, cyproconazole, epoxyconazole, hexaconazole, metconazole, propiconazole and tebuconazole;

molluscicides such as fentin acetate, metaldehyde, methiocarb, niclosamid, thiodicarb and trimethacarb;

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or conventional antifouling active compounds such as 4,5-dichloro-2-octyl-4-isothiazolin-3-one, diiodomethylparatryl sulfone, 2-(N,N-dimethylthiocarbamoylthio)-5-nitrothiazyl, potassium salts, copper salts, sodium salts and zinc salts of 2-pyridinethiol 1-oxide, pyridine-triphenylborane, tetrabutyldistannoxane, 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, 2,4,5,6-tetrachloroisophthalonitrile, tetramethylthiuram disulfide and 2,4,6-trichlorophenylmaleimide.

The antifouling compositions used comprise the active compound combinations according to the invention in a concentration of 0.001 to 50% by weight, in particular 0.01 to 20% by weight.

Moreover, the antifouling compositions according to the invention comprise the customary components such as, for example, those described in Ungerer, *Chem. Ind.* **1985**, *37*, 730-732 and Williams, Antifouling Marine Coatings, Noyes, Park Ridge, **1973**.

Besides the algicidal, fungicidal, molluscicidal active compounds and insecticidal active compounds according to the invention, antifouling paints comprise, in particular, binders.

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Examples of recognized binders are polyvinyl chloride in a solvent system, chlorinated rubber in a solvent system, acrylic resins in a solvent system, in particular in an aqueous system, vinyl chloride/vinyl acetate copolymer systems in the form of aqueous dispersions or in the form of organic solvent systems, butadiene/styrene/acrylonitrile rubbers, drying oils such as linseed oil, resin esters or modified hardened resins in combination with tar or bitumen, asphalt and epoxy compounds, small amounts of chlorine rubber, chlorinated polypropylene and vinyl resins.

If appropriate, paints also comprise inorganic pigments, organic pigments or colorants which are preferably insoluble in seawater. Paints may furthermore comprise materials such as colophonium to allow controlled release of the active compounds. Furthermore, the paints may comprise plasticizers, modifiers which affect the rheological properties and other conventional constituents. The compounds according to the invention or the abovementioned mixtures may also be incorporated into self-polishing antifouling systems.

- The active compound combinations are also suitable for controlling animal pests, in particular insects, arachnids and mites, which are found in enclosed spaces such as, for example, dwellings, factory halls, offices, vehicle cabins and the like. They can be employed in domestic insecticide products for controlling these pests. They are active against sensitive and resistant species and against all developmental stages. These pests include:
- From the order of the Scorpionidea, for example, Buthus occitanus.
 - From the order of the Acarina, for example, Argas persicus, Argas reflexus, Bryobia ssp., Dermanyssus gallinae, Glyciphagus domesticus, Ornithodorus moubat, Rhipicephalus sanguineus, Trombicula alfreddugesi, Neutrombicula autumnalis, Dermatophagoides pteronissimus, Dermatophagoides forinae.
- 25 From the order of the Araneae, for example, Aviculariidae, Araneidae.
 - From the order of the Opiliones, for example, Pseudoscorpiones chelifer, Pseudoscorpiones cheiridium, Opiliones phalangium.
 - From the order of the Isopoda, for example, Oniscus asellus, Porcellio scaber.
 - From the order of the Diplopoda, for example, Blaniulus guttulatus, Polydesmus spp.
- 30 From the order of the Chilopoda, for example, Geophilus spp.
 - From the order of the Zygentoma, for example, Ctenolepisma spp., Lepisma saccharina, Lepismodes inquilinus.
 - From the order of the Blattaria, for example, Blatta orientalies, Blattella germanica, Blattella asahinai, Leucophaea maderae, Panchlora spp., Parcoblatta spp., Periplaneta australasiae, Periplaneta
- 35 americana, Periplaneta brunnea, Periplaneta fuliginosa, Supella longipalpa.
 - From the order of the Saltatoria, for example, Acheta domesticus.

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From the order of the Dermaptera, for example, Forficula auricularia.

From the order of the Isoptera, for example, Kalotermes spp., Reticulitermes spp.

From the order of the Psocoptera, for example, Lepinatus spp., Liposcelis spp.

From the order of the Coleptera, for example, Anthrenus spp., Attagenus spp., Dermestes spp.,

5 Latheticus oryzae, Necrobia spp., Ptinus spp., Rhizopertha dominica, Sitophilus granarius, Sitophilus oryzae, Sitophilus zeamais, Stegobium paniceum.

From the order of the Diptera, for example, Aedes aegypti, Aedes albopictus, Aedes taeniorhynchus, Anopheles spp., Calliphora erythrocephala, Chrysozona pluvialis, Culex quinquefasciatus, Culex pipiens, Culex tarsalis, Drosophila spp., Fannia canicularis, Musca domestica, Phlebotomus spp.,

10 Sarcophaga camaria, Simulium spp., Stomoxys calcitrans, Tipula paludosa.

From the order of the Lepidoptera, for example, Achroia grisella, Galleria mellonella, Plodia interpunctella, Tinea cloacella, Tinea pellionella, Tineola bisselliella.

From the order of the Siphonaptera, for example, Ctenocephalides canis, Ctenocephalides felis, Pulex irritans, Tunga penetrans, Xenopsylla cheopis.

From the order of the Hymenoptera, for example, Camponotus herculeanus, Lasius fuliginosus, Lasius niger, Lasius umbratus, Monomorium pharaonis, Paravespula spp., Tetramorium caespitum. From the order of the Anoplura, for example, Pediculus humanus capitis, Pediculus humanus corporis, Phthirus pubis.

From the order of the Heteroptera, for example, Cimex hemipterus, Cimex lectularius, Rhodnius prolixus, Triatoma infestans.

They are used as aerosols, pressureless spray products, for example pump and atomizer sprays, automatic fogging systems, foggers, foams, gels, evaporator products with evaporator tablets made of cellulose or polymer, liquid evaporators, gel and membrane evaporators, propeller-driven evaporators, energy-free, or passive, evaporation systems, moth papers, moth bags and moth gels, as granules or dusts, in baits for spreading or in bait stations.

According to the invention, it is possible to treat all plants and parts of plants. Plants are to be understood here as meaning all plants and plant populations such as desired and undesired wild plants or crop plants (including naturally occurring crop plants). Crop plants can be plants which can be obtained by conventional breeding and optimization methods or by biotechnological and genetic engineering methods or combinations of these methods, including the transgenic plants and including the plant cultivars which can or cannot be protected by plant breeders' certificates. Parts of plants are to be understood as meaning all above-ground and below-ground parts and organs of plants, such as shoot, leaf, flower and root, examples which may be mentioned being leaves, needles, stems, trunks, flowers, fruit-bodies, fruits and seeds and also roots, tubers and rhizomes. Parts of plants also include

harvested plants and vegetative and generative propagation material, for example seedlings, tubers, rhizomes, cuttings and seeds.

The treatment according to the invention of the plants and parts of plants with the active compounds is carried out directly or by action on their environment, habitat or storage area according to customary treatment methods, for example by dipping, spraying, evaporating, atomizing, broadcasting, brushing-on and, in the case of propagation material, in particular in the case of seeds, furthermore by one- or multi-layer coating.

As already mentioned above, it is possible to treat all plants and their parts according to the invention.

In a preferred embodiment, wild plant species and plant cultivars, or those obtained by conventional biological breeding methods, such as crossing or protoplast fusion, and parts thereof, are treated. In a further preferred embodiment, transgenic plants and plant cultivars obtained by genetic engineering methods, if appropriate in combination with conventional methods (Genetically Modified Organisms), and parts thereof are treated. The terms "parts", "parts of plants" and "plant parts" have been explained above.

Particularly preferably, plants of the plant cultivars which are in each case commercially available or in use are treated according to the invention.

- Depending on the plant species or plant cultivars, their location and growth conditions (soils, climate, vegetation period, diet), the treatment according to the invention may also result in superadditive ("synergistic") effects. Thus, for example, reduced application rates and/or a widening of the activity spectrum and/or an increase in the activity of the substances and compositions which can be used according to the invention, better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to water or soil salt content, increased flowering performance, easier harvesting, accelerated maturation, higher harvest yields, better quality and/or a higher nutritional value of the harvested products, better storage stability and/or processability of the harvested products are possible which exceed the effects which were actually to be expected.
- The transgenic plants or plant cultivars (i.e. those obtained by genetic engineering) which are preferred and to be treated according to the invention include all plants which, in the genetic modification, received genetic material which imparts particularly advantageous useful traits to these plants. Examples of such traits are better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to water or soil salt content, increased flowering performance, easier harvesting, accelerated maturation, higher harvest yields, better quality and/or a

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higher nutritional value of the harvested products, better storage stability and/or processability of the harvested products. Further and particularly emphasized examples of such properties are a better defense of the plants against animal and microbial pests, such as against insects, mites, phytopathogenic fungi, bacteria and/or viruses, and also increased tolerance of the plants to certain herbicidally active compounds. Examples of transgenic plants which may be mentioned are the important crop plants, such as cereals (wheat, rice), corn, soya beans, potatoes, cotton, tobacco, oilseed rape and also fruit plants (with the fruits apples, pears, citrus fruits and grapes), and particular emphasis is given to corn, soya beans, potatoes, cotton, tobacco and oilseed rape. Traits that are particularly emphasized are the increased defense of the plants against insects, arachnids, nematodes and slugs and snails by toxins formed in the plants, in particular those formed by the genetic material from Bacillus thuringiensis (for example by the genes CryIA(a), CryIA(b), CryIA(c), CryIIA, CryIIIA, CryIIIB2, Cry2Ab, Cry3Bb and CryIF and also combinations thereof) (hereinbelow referred to as "Bt plants"). Traits that are also particularly emphasized are the increased defense of the plants against fungi, bacteria and viruses by Systemic Acquired Resistance (SAR), systemin, phytoalexins, elicitors, as well as resistance genes and correspondingly expressed proteins and toxins. Traits that are furthermore particularly emphasized are the increased tolerance of the plants to certain herbicidally active compounds, for example imidazolinones, sulfonylureas, glyphosate or phosphinotricin (for example the "PAT" gene). The genes in question which impart the desired traits can also be present in combination with one another in the transgenic plants. Examples of "Bt plants" which may be mentioned are corn varieties, cotton varieties, soya bean varieties and potato varieties which are sold under the trade names YIELD GARD® (for example corn, cotton, soya beans), KnockOut® (for example corn), StarLink® (for example corn), Bollgard® (cotton), Nucotn® (cotton) and NewLeaf® (potato). Examples of herbicide-tolerant plants which may be mentioned are corn varieties, cotton varieties and soya bean varieties which are sold under the trade names Roundup Ready® (tolerance to glyphosate, for example corn, cotton, soya bean), Liberty Link® (tolerance to phosphinotricin, for example oilseed rape), IMI® (tolerance to imidazolinones) and STS® (tolerance to sulfonylureas, for example corn). Herbicide-resistant plants (plants bred in a conventional manner for herbicide tolerance) which may be mentioned include the varieties sold under the name Clearfield® (for example corn). Of course, these statements also apply to plant cultivars having these or still-to-be-developed genetic traits, which plants will be developed and/or marketed in the future.

The plants listed can be treated according to the invention in a particularly advantageous manner with the active compound mixtures according to the invention. The preferred ranges stated above for the mixtures also apply to the treatment of these plants. Particular emphasis is given to the treatment of plants with the mixtures specifically mentioned in the present text.

The good insecticidal and acaricidal action of the active compound combinations according to the invention can be seen from the examples which follow. While the individual active compounds show weaknesses in their action, the combinations show an action which exceeds a simple sum of actions.

A synergistic effect in insecticides and acaricides is always present when the action of the active compound combinations exceeds the total of the actions of the active compounds when applied individually.

The expected action for a given combination of two active compounds can be calculated as follows, according to S.R. Colby, Weeds <u>15</u> (1967), 20-22:

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If

X is the kill rate, expressed as a percentage of the untreated control, when employing active compound A at an application rate of m g/ha or in a concentration of m ppm,

Y is the kill rate, expressed as a percentage of the untreated control, when employing active compound B at an application rate of <u>n</u> g/ha or in a concentration of <u>n</u> ppm and

E is the kill rate, expressed as a percentage of the untreated control, when employing active compounds A and B at application rates of \underline{m} and \underline{n} g/ha or in a concentration of \underline{m} and \underline{n} ppm,

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$$E=X+Y-\frac{X\cdot Y}{100}$$

If the actual insecticidal kill rate exceeds the calculated value, the action of the combination is superadditive, i.e. a synergistic effect is present. In this case, the actually observed kill rate must exceed the value calculated using the above formula for the expected kill rate (E).

After the desired period of time, the kill in % is determined. 100% means that all animals have been killed; 0% means that none of the animals have been killed.

Use examples

Example A

5 Myzus persicae test

Solvent:

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7 parts by weight of dimethylformamide

Emulsifier:

2 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

Cabbage leaves (*Brassica oleracea*) which are heavily infested by the green peach aphid (*Myzus* persicae) are treated by being dipped into the preparation of active compound of the desired concentration.

After the desired period of time, the kill in % is determined. 100% means that all aphids have been killed; 0% means that none of the aphids have been killed. The kill rates determined are calculated using Colby's formula (see page 30).

In this test, for example, the following active compound combination in accordance with the present application shows a synergistically enhanced activity compared to the active compounds applied on their own:

Table A1: Plant-damaging insects

Myzus persicae test

Active compounds	Concentration of active compound in ppm	Kill rate in % after 6 ^d	
		found*	calc.**
H_3C H_3C O	4	15	
Br H ₃ C CH ₃ O CN (2-6) deltamethrin	0.16	50	
(I-1-9) + (2-6) deltamethrin (25:1)	4 + 0.16	80	57.5

* found

= activity found

** calc.

= activity calculated using Colby's formula

Table A2: Plant-damaging insects

Myzus persicae test

Active compounds	Concentration of active compound in ppm	Kill ra afte	te in % r 6 ^d
		found*	calc.**
H_3C H_3C H_3C O N O	0.8	0	
H ₃ C CN CN CN CN CN CN CON CON CON CON CON	0.032	0	
(I-1-9) + (2-12) lambda-cyhalothrin (25:1)	0.8 + 0.032	45	0

* found

= activity found

** calc.

= activity calculated using Colby's formula

Example B

Phaedon cochleariae larvae test

5 Solvent:

7 parts by weight of dimethylformamide

Emulsifier:

2 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

Cabbage leaves (*Brassica oleracea*) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with larvae of the mustard beetle (*Phaedon cochleariae*) while the leaves are still moist.

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After the desired period of time, the kill in % is determined. 100% means that all beetle larvae have been killed; 0% means that none of the beetle larvae have been killed. The kill rates determined are calculated using Colby's formula (see page 30).

In this test, the following active compound combination in accordance with the present application showed a synergistically enhanced activity compared to the active compounds applied on their own:

Table B: Plant-damaging insects **Phaedon cochleariae larvae test**

Active compounds	Concentration of active compound in ppm	Kill rate in % after 3 ^d	
		found*	calc.**
H_3C H_3C O	0.16	0	
NC O H ₃ C CH ₃ CI CI (2-3) betracyfluthrin	0.16	15	
(I-1-9) + (2-3) betracyfluthrin (1:1)	0.16 + 0.16	35	15

found

= activity found = activity calculated using Colby's formula

calc.

Example C

Plutella-xylostella test (resistant strain)

5 Solvent:

7 parts by weight of dimethylformamide

Emulsifier:

2 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

Cabbage leaves (*Brassica oleracea*) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with caterpillars of the diamond back moth (*Plutella xylostella*, resistant strain), while the leaves are still moist.

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After the desired period of time, the kill in % is determined. 100% means that all caterpillars have been killed; 0% means that none of the caterpillars have been killed. The kill rates determined are calculated using Colby's formula (see page 30).

In this test, the following active compound combination in accordance with the present application showed a synergistically enhanced activity compared to the active compounds applied on their own:

Table C1: Plant-damaging insects
Plutella-xylostella test (resistant strain)

Active compounds	Concentration of active compound in ppm	Kill rate in % after 6 ^d	
		found*	calc.**
H_3C H_3C O	0.0064	0	
NC O CH ₃ CH ₃ CH ₃ (2-3) betracyfluthrin	0.0064	0	
(I-1-9) + (2-3) betracyfluthrin (1:1)	0.0064 + 0.0064	35	0

* found

= activity found

** calc.

= activity calculated using Colby's formula

Table C2: Plant-damaging insects
Plutella-xylostella test (resistant strain)

Active compounds	Concentration of active compound in ppm	Kill rate in % after 6 ^d	
		found*	calc.**
H_3C H_3C O	0.0064	10	
CI F ₃ C (2-12) lambda-cyhalothrin	0.0064	0	
(I-1-9) + (2-12) lambda-cyhalothrin (1:1)	0.0064 + 0.0064	45	10

* found

= activity found

** calc.

= activity calculated using Colby's formula

Example D

Spodoptera frugiperda test

5 Solvent:

7 parts by weight of dimethylformamide

Emulsifier:

2 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

Cabbage leaves (*Brassica oleracea*) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with caterpillars of the armyworm (*Spodoptera frugiperda*), while the leaves are still moist.

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After the desired period of time, the kill in % is determined. 100% means that all caterpillars have been killed; 0% means that none of the caterpillars have been killed. The kill rates determined are calculated using Colby's formula (see page 30).

In this test, the following active compound combination in accordance with the present application showed a synergistically enhanced activity compared to the active compounds applied on their own:

Table D: Plant-damaging insects Spodoptera frugiperda test

Active compounds	Concentration of active compound in ppm	Kill rate in % after 6 ^d	
		found*	calc.**
H_3C H H_3C O	0.032	75	
NC O H ₃ C CH ₃ Cl Cl (2-3) betracyfluthrin	0.032	0	
(I-1-9) + (2-3) betracyfluthrin (1:1)	0.032 + 0.032	100	75

found

= activity found

** calc.

= activity calculated using Colby's formula

Claims

1. A composition comprising a synergistically effective active compound combination of anthranilamides of the formula (I)

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in which

A¹ and A² independently of one another represent oxygen or sulfur,

 X^1 represents N or CR^{10} ,

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R¹ represents hydrogen or represents in each case optionally mono- or polysubstituted C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl or C₃-C₆-cycloalkyl, where the substituents independently of one another may be selected from the group consisting of R⁶, halogen, cyano, nitro, hydroxyl, C₁-C₄-alkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₂-C₄-alkoxycarbonyl, C₁-C₄-alkylamino, C₂-C₈-dialkylamino, C₃-C₆-cycloalkylamino, (C₁-C₄-alkyl)C₃-C₆-cycloalkylamino and R¹¹.

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 R^2 represents hydrogen, C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl, C_3 - C_6 -cycloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -alkylamino, C_2 - C_8 -dialkylamino, C_3 - C_6 -cycloalkylamino, C_2 - C_6 -alkoxycarbonyl or C_2 - C_6 -alkylcarbonyl,

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represents hydrogen, R¹¹ or represents in each case optionally mono- or polysubstituted C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, C₃-C₆-cycloalkyl, where the substituents independently of one another may be selected from the group consisting of R⁶, halogen, cyano, nitro, hydroxyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₂-C₆-alkoxycarbonyl, C₂-C₆-alkylcarbonyl, C₃-C₆-trialkylsilyl, R¹¹, phenyl, phenoxy and a 5- or 6-membered heteroaromatic ring, where each phenyl, phenoxy and 5- or 6-membered heteroaromatic ring may optionally be substituted and where the substituents independently of one another may be selected from one to three radicals W or one or more radicals R¹², or

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R² and R³ may be attached to one another and form the ring M,

 R^4 represents hydrogen, C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, C₃-C₆-cycloalkyl, C₁-C₆-haloalkyl, C₂-C₆-haloalkenyl, C₂-C₆-haloalkynyl, C₃-C₆-halocycloalkyl, halogen, cyano, nitro, hydroxyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-haloalkylthio, C₁-C₄-haloalkylsulfinyl, C₁-C₄-haloalkylsulfonyl, C₁-C₄-alkylamino, C₂-C₈-dialkylamino, C₃-C₆cycloalkylamino, C₃-C₆-trialkylsilyl or represents in each case optionally mono- or polysubstituted phenyl, benzyl or phenoxy, where the substituents independently of one another may be selected from the group consisting of C₁-C₄-alkyl, C₂-C₄alkenyl, C₂-C₄-alkynyl, C₃-C₆-cycloalkyl, C₁-C₄-haloalkyl, C₂-C₄-haloalkenyl, C₂-C₄-haloalkynyl, C₃-C₆-halocycloalkyl, halogen, cyano, nitro, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-C₂-C₈-dialkylamino, C_3 - C_6 -cycloalkylamino, alkylamino, C_3 - C_6 -(alkyl)-C₂-C₄-alkylcarbonyl, C₂-C₆-alkoxycarbonyl, C₂-C₆-alkylcycloalkylamino, aminocarbonyl, C₃-C₈-dialkylaminocarbonyl and C₃-C₆-trialkylsilyl,

R⁵ and R⁸ in each case independently of one another represent hydrogen, halogen or represent in each case optionally substituted C₁-C₄-alkyl, C₁-C₄-haloalkyl, R¹², G, J, -OJ, -OG, -S(O)_p-J, -S(O)_p-G, -S(O)_p-phenyl, where the substituents independently of one another may be selected from one to three radicals W or from the group consisting of R¹², C₁-C₁₀-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, C₁-C₄-alkoxy and C₁-C₄-alkythio, where each substituent may be substituted by one or more substituents independently of one another selected from the group consisting of G, J, R⁶, halogen, cyano, nitro, amino, hydroxyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-haloalkylthio, C₁-C₄-haloalkylsulfinyl, C₁-C₄-haloalkylsulfonyl, C₁-C₄-alkylamino, C₂-C₈-dialkylamino, C₃-C₆-trialkylsilyl, phenyl and phenoxy, where each phenyl or phenoxy ring may optionally be substituted and where the substituents independently of one another may be selected from one to three radicals W or one or more radicals R¹²,

in each case independently of one another represent a 5- or 6-membered nonaromatic carbocyclic or heterocyclic ring which optionally contains one or two ring members from the group consisting of C(=O), SO and $S(=O)_2$ and which may optionally be substituted by one to four substituents independently of one another selected from the group consisting of C_1 - C_2 -alkyl, halogen, cyano, nitro and C_1 - C_2 -alkoxy, or independently of one another represent C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl, C_3 - C_7 -cycloalkyl, (cyano) C_3 - C_7 -cycloalkyl, (C_1 - C_4 -alkyl) C_3 - C_6 -cycloalkyl, (C_3 - C_6 - C_6 -cycloalkyl, (C_3 - C_6 -

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cycloalkyl)C₁-C₄-alkyl, where each cycloalkyl, (alkyl)cycloalkyl and (cycloalkyl)alkyl may optionally be substituted by one or more halogen atoms. J in each case independently of one another represent an optionally substituted 5- or 6-membered heteroaromatic ring, where the substituents independently of one 5 another may be selected from one to three radicals W or one or more radicals R¹². independently of one another represent $-C(=E^1)R^{19}$, $-LC(=E^1)R^{19}$, $-C(=E^1)LR^{19}$, R^6 -OP(=Q)(OR 19)₂, -SO₂LR 18 or -LSO₂LR 19 , where each E¹ $-LC(=E^{1})LR^{19}$, independently of the others represents O, S, N-R¹⁵, N-OR¹⁵, N-N(R¹⁵)₂, N-S=O, N-CN or N-NO2, \mathbb{R}^7 10 represents hydrogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, halogen, C₁-C₄-alkoxy, C₁-C₄haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-haloalkylthio, C₁-C₄-haloalkylsulfinyl, C₁-C₄-haloalkylsulfonyl, R9 represents C₁-C₄-haloalkyl, C₁-C₄-haloalkoxy, C₁-C₄-haloalkylsulfinyl or halogen, R^{10} represents hydrogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, halogen, cyano or C₁-C₄-halo-15 alkoxy, R^{11} in each case independently of one another represent in each case optionally monoto trisubstituted C₁-C₆-alkylthio, C₁-C₆-alkylsulfenyl, C₁-C₆-haloalkythio, C₁-C₆haloalkylsulfenyl, phenylthio or phenylsulfenyl, where the substituents independently of one another may be selected from the list consisting of W, 20 $-S(O)_{n}N(R^{16})_{2}$ $-C(=O)R^{13}$, $-L(C=O)R^{14}$, $-S(C=O)LR^{14}$ $-C(=O)LR^{13}$. $-S(O)_nNR^{13}C(=O)R^{13}$, $-S(O)_nNR^{13}C(=O)LR^{14}$ and $-S(O)_nNR^{13}S(O)_2LR^{14}$, L in each case independently of one another represent O, NR¹⁸ or S, R^{12} in each case independently of one another represent -B(OR¹⁷)₂, amino, SH, thiocyanato, C_3 - C_8 -trialkylsilyloxy, C_1 - C_4 -alkyl disulfide, -SF₅, -C(=E) \mathbb{R}^{19} , $-LC(=E)R^{19}$, $-C(=E)LR^{19}$, $-LC(=E)LR^{19}$, $-OP(=Q)(OR^{19})_2$, $-SO_2LR^{19}$ or 25 -LSO₂LR¹⁹, Q represents O or S, R^{13} in each case independently of one another represent hydrogen or represent in each case optionally mono- or polysubstituted C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl 30 or C₃-C₆-cycloalkyl, where the substituents independently of one another may be selected from the group consisting of R⁶, halogen, cyano, nitro, hydroxyl, C₁-C₄alkoxy, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-alkylamino, C₂-C₈-dialkylamino, C₃-C₆-cycloalkylamino and (C₁-C₄-alkyl)C₃-C₆-cycloalkylamino, R^{14} in each case independently of one another represent in each case mono- or 35 polysubstituted C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₂-C₂₀-alkynyl or C₃-C₆-cycloalkyl,

where the substituents independently of one another may be selected from the

 R^{15}

 R^{17}

group consisting of R⁶, halogen, cyano, nitro, hydroxyl, C₁-C₄-alkoxy, C₁-C₄alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-alkylamino, C₂-C₈-dialkylamino, C₃-C₆cycloalkylamino and (C₁-C₄-alkyl)C₃-C₆-cycloalkylamino or represent optionally substituted phenyl, where the substituents independently of one another may be selected from one to three radicals W or one or more radicals R¹²,

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in each case independently of one another represent hydrogen or represent in each case mono- or polysubstituted C₁-C₆-haloalkyl or C₁-C₆-alkyl, where the substituents independently of one another may be selected from the group consisting of cyano, nitro, hydroxyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-haloalkylthio, C₁-C₄haloalkylsulfinyl, C₁-C₄-haloalkylsulfonyl, C₁-C₄-alkylamino, C₂-C₈-dialkylamino, C₂-C₆-alkoxycarbonyl, C₂-C₆-alkylcarbonyl, C₃-C₆-trialkylsilyl and optionally substituted phenyl, where the substituents independently of one another may be selected from one to three radicals W or one or more radicals R¹², or N(R¹⁵)₂ represents a cycle which forms the ring M,

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 R^{16} represents C₁-C₁₂-alkyl or C₁-C₁₂-haloalkyl, or N(R¹⁶)₂ represents a cycle which forms the ring M,

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in each case independently of one another represent hydrogen or C₁-C₄-alkyl, or B(OR¹⁷)₂ represents a ring, where the two oxygen atoms are attached via a chain to two or three carbon atoms which are optionally substituted by one or two substituents independently of one another selected from the group consisting of methyl and C₂-C₆-alkoxycarbonyl,

 R^{18} in each case independently of one another represent hydrogen, C₁-C₆-alkyl or C₁-C₆-haloalkyl, or N(R¹³)(R¹⁸) represents a cycle which forms the ring M,

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 R^{19} in each case independently of one another represent hydrogen or represent in each case optionally mono- or polysubstituted C₁-C₆-alkyl, where the substituents independently of one another may be selected from the group consisting of cyano, nitro, hydroxyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-haloalkylthio, C₁-C₄-haloalkylsulfinyl, C₁-C₄haloalkylsulfonyl, C₁-C₄-alkylamino, C₂-C₈-dialkylamino, CO₂H, C₂-C₆-alkoxycarbonyl, C2-C6-alkylcarbonyl, C3-C6-trialkylsilyl and optionally substituted phenyl, where the substituents independently of one another may be selected from one to three radicals W, C₁-C₆-haloalkyl, C₃-C₆-cycloalkyl or phenyl or pyridyl, each of which is optionally mono- to trisubstituted by W,

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in each case represents an optionally mono- to tetrasubstituted ring which, in addition to the nitrogen atom which is attached to the substituent pair R¹³ and R¹⁸,

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M

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 $(R^{15})_2$ or $(R^{16})_2$, contains two to six carbon atoms and optionally additionally a further nitrogen, sulfur or oxygen atom, and where the substituents independently of one another may be selected from the group consisting of C_1 - C_2 -alkyl, halogen, cyano, nitro and C_1 - C_2 -alkoxy,

W in each case independently of one another represent C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₃-C₆-cycloalkyl, C₁-C₄-haloalkyl, C₂-C₄-haloalkenyl, C₂-C₄-haloalkynyl, C₃-C₆-halocycloalkyl, halogen, cyano, nitro, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-alkylsulfinyl, C₁-C₄-alkylsulfonyl, C₁-C₄-alkylamino, C₂-C₆-dialkylamino, C₃-C₆-cycloalkylamino, (C₁-C₄-alkyl)C₃-C₆-cycloalkylamino, C₂-C₄-alkylcarbonyl, C₂-C₆-alkoxycarbonyl, CO₂H, C₂-C₆-alkylaminocarbonyl, C₃-C₈-dialkylaminocarbonyl or C₃-C₆-trialkylsilyl,

- n in each case independently of one another represent 0 or 1,
- p in each case independently of one another represent 0, 1 or 2,

where in the case that (a) R⁵ represents hydrogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₂-C₆-haloalkynyl, C₁-C₄-haloalkynyl, C₁-C₄-haloalkylthio or halogen and (b) R⁸ represents hydrogen, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₂-C₆-haloalkenyl, C₂-C₆-haloalkynyl, C₁-C₄-haloalkoxy, C₁-C₄-haloalkylthio, halogen, C₂-C₄-alkylcarbonyl, C₂-C₆-alkoxycarbonyl, C₂-C₆-alkylaminocarbonyl or C₃-C₈ dialkylaminocarbonyl, (c) at least one substituent selected from the group consisting of R⁶, R¹¹ and R¹² is present and (d), if R¹² is not present, at least one R⁶ or R¹¹ is different from C₂-C₆-alkylcarbonyl, C₂-C₆ alkoxycarbonyl, C₂-C₆-alkylaminocarbonyl and C₃-C₈-dialkylaminocarbonyl, and

the compounds of the general formula (I) also include N-oxides and salts,

and at least one active compound from the group of the pyrethroids (active compounds of group 2) is synergistically effective and suitable for controlling animal pests.

2. The composition as claimed in claim 1 comprising at least one active compound from the group of the anthranilamides of the formula (I-1) in which

$$R^3$$
 N N R^7 R^4 O N N N R^9

in which

R² represents hydrogen or C₁-C₆-alkyl,

R³ represents C₁-C₆-alkyl which is optionally substituted by a radical R⁶,

R⁴ represents C₁-C₄-alkyl, C₁-C₂-haloalkyl, C₁-C₂-haloalkoxy or halogen,

R⁵ represents hydrogen, C₁-C₄-alkyl, C₁-C₂-haloalkyl, C₁-C₂-haloalkoxy or halogen,

 R^6 represents $-C(=E^2)R^{19}$, $-LC(=E^2)R^{19}$, $-C(=E^2)LR^{19}$ or $-LC(=E^2)LR^{19}$, where each E^2 independently of the others represents O, S, N-R¹⁵, N-OR¹⁵, N-N(R¹⁵)₂, and each L independently of the others represents O or NR¹⁸,

R⁷ represents C₁-C₄-haloalkyl or halogen,

10 R⁸ represents hydrogen,

 R^9 represents C_1 - C_2 -haloalkyl, C_1 - C_2 -haloalkoxy, $S(O)_pC_1$ - C_2 -haloalkyl or halogen,

 R^{15} in each case independently of one another represent hydrogen or represent in each case optionally substituted C_1 - C_6 -haloalkyl or C_1 - C_6 -alkyl, where the substituent independently of one another may be selected from the group consisting of cyano, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio, C_1 - C_4 -alkylsulfinyl, C_1 - C_4 -haloalkylthio, C_1 - C_4 -haloalkylsulfinyl or C_1 - C_4 -haloalkylsulfonyl,

R¹⁸ in each case represents hydrogen or C₁-C₄-alkyl,

R¹⁹ in each case independently of one another represent hydrogen or C₁-C₆-alkyl,

p independently of one another represents 0, 1, 2.

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3. The composition as claimed in claim 1 or 2 comprising at least one active compound from the group of the pyrethroids (active compounds of group 2) selected from

(2-1) acrinathrin

25 and/or

(2-2) alpha-cypermethrin

and/or

(2-3) betacyfluthrin

and/or

(2-4) cyhalothrin

5 and/or

(2-5) cypermethrin

and/or

(2-6) deltamethrin

10

and/or

(2-7) esfenvalerate

and/or

15 (2-8) ethofenprox

and/or

(2-9) fenpropathrin

$$\begin{array}{c|c} H_3C & CH_3 \\ \hline \\ H_3C & CH_3 & O \\ \hline \end{array}$$

and/or

(2-10) fenvalerate

and/or

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(2-11) flucythrinate

and/or

10 (2-12) lambda-cyhalothrin

and/or

(2-13) permethrin

15 and/or

(2-14) taufluvalinate

and/or

(2-15) tralomethrin

$$\mathsf{Br_3C} \bigvee_{\mathsf{Br}}^{\mathsf{H_3C}} \mathsf{CH_3} \\ \mathsf{O} \bigvee_{\mathsf{CN}} \mathsf{O} \bigvee_{\mathsf{O}} \mathsf{O}$$

and/or

(2-16) zeta-cypermethrin

5 and/or

(2-17) cyfluthrin

and/or

(2-18) bifenthrin

10

and/or

(2-19) cycloprothrin

and/or

15 (2-20) eflusilanate

and/or

(2-21) fubfenprox

and/or

(2-22) pyrethrin

$$\mathsf{R}^{20} \underbrace{\mathsf{CH}_{3}}^{\mathsf{H}_{3}\mathsf{C}} \underbrace{\mathsf{CH}_{3}}_{\mathsf{O}} \underbrace{\mathsf{H}_{3}\mathsf{C}}_{\mathsf{C}} \underbrace{\mathsf{CH}_{2}}_{\mathsf{C}} \underbrace{\mathsf{H}_{2}}_{\mathsf{R}^{21}}$$

 $R^{20} = -CH_3 \text{ or } -CO_2CH_3$

$$R^{21} = -CH = CH_2 \text{ or } -CH_3 \text{ or } -CH_2CH_3$$

and/or

(2-23) resmethrin

10 and/or

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(2-24) gamma-cyhalothrin

- 4. The composition as claimed in claim 1, 2 or 3 comprising anthranilamides of the formula

 (I) and at least one pyrethroid (group 2) in a ratio of from 50:1 to 1:5.
 - 5. The use of a synergistically effective mixture comprising compounds of the formula (I) as set forth in claim 1 or 2 and at least one pyrethroid (group 2) for controlling animal pests.
- A process for preparing pesticides, characterized in that a synergistically effective mixture comprising compounds of the formula (I) as set forth in claim 1 or 2 and at least one pyrethroid (group 2) are mixed with extenders and/or surfactants.

Combination of active substance with insecticidal properties

Abstract

The invention relates to novel insecticidal active compound combinations consisting, firstly, of anthranilamides and, secondly, of further insecticidally active compounds from the group of the pyrethroids, which combinations are highly suitable for controlling animal pests, such as insects.